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**Azo-Carbazole Polymethacrylates as Single-Component Electro-Optic  
Materials**

by

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# Azo-Carbazole Polymethacrylates as Single-Component Electro-Optic Materials

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## Abstract

A series of amorphous azobenzene and carbazole-containing polymers was prepared, which incorporates both electro-optic activity and photoconductivity into a single multifunctional structural unit. The polymers were cast as thin films, and were shown to be suitable for photoinducing birefringence reversibly with polarized light, as well as for the inscription of photorefractive diffraction gratings after electric field poling. Since the polymer series encompasses a range of spacer lengths (from 3 to 10 methylene groups) between the multifunctional side chains and the polymer backbone, these materials are suitable for study of the influence of chromophore mobility on these optical phenomena. The extent of orientational order which could be photoinduced in the films was found to decrease with increasing spacer

length, as did the photoconductivity and the photorefractive two-beam optical coupling gain. In thin films of polymers with the highest glass transition temperature, a birefringence of 0.065 could be photoinduced, with a time constant of  $<0.8$  seconds. A two-beam optical gain of  $0.024 \mu\text{m}^{-1}$  was also demonstrated in films of the polymer with the highest glass transition temperature, although this gain was exceeded by absorption losses.

## Introduction

Polymers which incorporate both photoconductive and electro-optic functionalities can be regarded as suitable materials for a wide range of optical and electro-optic applications. If the electro-optic (EO) chromophores are based on an azobenzene structure, these groups can be preferentially oriented with a polarized laser for reversible optical storage,<sup>1,2</sup> and for the inscription of channel waveguides.<sup>3,4</sup> In addition, thin films of these azobenzene-based chromophores have been shown to be suitable for the laser inscription of high efficiency surface relief diffraction gratings.<sup>5,6</sup> Systems which can be poled and possess both photoconductivity and a sufficient EO response can also be suitable for the inscription of photorefractive (PR) gratings.<sup>7-9</sup> With diffraction efficiencies which can approach 100%,<sup>10</sup> and grating inscription times which can be as brief as 60 ms,<sup>11</sup> poled photorefractive polymers have now begun to perform competitively with traditional inorganic crystals, and they possess some advantages such as lower cost, greater versatility, and relative ease of preparation and processing.

It is usually an advantage with multi-functional polymers if the individual components are incorporated in as high a concentration as possible, both for optimal performance and for increased efficiency. Hence, there has been much interest in materials which combine the photoconductive and EO components into a single multi-functional structural unit.<sup>12-16</sup> It can also be a distinct advantage (for optical purity and for thermal stability) if this single multi-functional unit is bound to the polymer backbone, and for this reason there has been recent interest in fully-functionalized multi-component polymer systems.<sup>17,18</sup>

In a previous report,<sup>17</sup> thin films of a novel side chain azobenzene-carbazole polymer were shown to be suitable materials for reversibly photoinducing birefringence, for inscribing high efficiency surface relief gratings, and for storage of a photorefractive grating. This azo-carbazole single-component multi-functional side group was bound to a methacrylate backbone with a short ethylene spacer. While this produced a high (>165 °C) glass transition temperature ( $T_g$ ) material which exhibited high thermal stability, the mobility of the side chains was necessarily limited. Since all of the optical phenomena reported require mobility for optimal performance, the material with the highest  $T_g$  is not necessarily optimal, as there is a trade off between ease of induced orientation, and retention of induced order over time due to thermal relaxations.

In this paper the preparation and optical characterization of a series of multi-functional single-component polymers based on this azo-carbazole structure is described, where the distance between the chromophore and the methacrylate main chain is systematically increased by the number of methylene groups in the spacer (from 3 to 10). Photoinduced birefringence and photorefractivity are studied with polymers of this series as a function of its structure.

## Experimental Section

Proton spectra were recorded on a Bruker AC-F 200 NMR spectrometer. The molecular weight of the polymers (relative to polystyrene) was determined with a Waters Associates Liquid Chromatograph equipped with  $\mu$ -styragel columns and a R401 differential refractometer. The glass transition temperatures ( $T_g$ ) were determined with a Mettler TA 3000 thermal analysis system equipped with TC10A TA processor and DSC30 head. Cast films were determined to be amorphous by polarized microscopy using a Nikon Labophot-2 microscope equipped with a Leitz heating stage, and the electronic spectra of the films were recorded with a Shimadzu TR-280 UV-visible spectrophotometer. The preparation of the materials is summarized in Scheme 1.

### SCHEME 1.

#### Preparation of N-[ $\omega$ -(bromoalkyl)]carbazoles (**1a-1g**):

To a mixture of carbazole (5.0 g, 30 mmol), benzene (15 ml), benzyltriethylammonium chloride (BTEAC) (250 mg) and aqueous (50%) sodium hydroxide solution (15 ml), an excess amount (greater than ten-fold equivalent to carbazole) of alkyl dibromide was added under stirring.

**N-(3'-Bromopropyl) Carbazole (1a).** Yield: 91%, mp 124 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.12 (m, 2H); 3.62 (t, 2H); 4.48 (t, 2H); 7.20-7.30 (m, 2H); 7.45 (m, 4H); 8.09 (m, 2H).

**N-(4'-Bromobutyl) Carbazole (1b).** Yield: 88%, mp 107 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.80-2.20 (m, 4H); 3.37 (t, 2H); 4.34 (t, 2H); 7.18-7.29 (m, 2H); 7.46-7.51 (m, 4H); 8.10 (m, 2H).

**N-(5'-Bromopentyl) Carbazole (1c).** Yield: 76%, mp 72 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.52 (m, 4H); 1.86 (m, 4H); 3.34 (t, 2H); 4.27 (t, 2H); 7.18-7.31 (m, 2H); 7.33-7.51 (m, 4H); 8.11 (m, 2H).

**N-(6'-Bromohexyl) Carbazole (1d).** Yield: 70%, mp 58 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.31-1.55 (m, 4H); 1.73-1.95 (m, 4H); 3.35 (t, 2H); 4.30 (t, 2H); 7.17-7.26 (m, 2H); 7.32-7.50 (m, 4H); 8.95 (m, 2H).

**N-(8'-Bromooctyl) Carbazole (1e).** Yield: 66%, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.20-1.46 (m, 8H); 1.75-1.98 (m, 4H); 3.38 (t, 2H); 4.31 (t, 2H); 7.21-7.28 (m, 2H); 7.38-7.55 (m, 4H); 8.12 (m, 2H).

**N-(9'-Bromononyl) Carbazole (1f).** Yield: 65%, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.20-1.55 (m, 10H); 1.76-1.95 (m, 4H); 3.39 (t, 2H); 4.26 (t, 2H); 7.20-7.35 (m, 2H); 7.36-7.57 (m, 4H); 8.13 (m, 2H).

**N-(10'-Bromodecyl) Carbazole (1g).** Yield: 78%, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.18-1.26 (m, 12H); 1.72-1.79 (m, 4H); 3.32 (t, 2H); 4.28 (t, 2H); 7.16-7.40 (m, 6H); 8.03 (d, 2H).

#### **Preparation of N-[ω-(Methacryloxy)alkyl] Carbazoles (2a-2g):**

A mixture of N-(ω'-bromoalkyl) carbazole (32.1 mmol) in chloroform (75 ml), tetrabutylammonium bromide (2.1g, 7.5 mmol) and an aqueous solution (25 ml) of sodium methacrylate (14.0 g, 129.1 mmol) containing a trace amount of hydroquinone was stirred at 55 °C for 48 hours. The organic layer was extracted with chloroform, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography. The pure products were obtained by removing the solvent under reduced pressure.

**N-[3'-(Methacryloxy)propyl] Carbazole (2a).** Yield: 72%, mp 45 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.93 (s, 3H); 2.24 (q, 2H); 4.15 (t, 2H); 4.43 (t, 2H); 5.56 (m, 1H); 6.12 (m, 1H); 7.19-7.28 (m, 2H); 7.37-7.51 (m, 4H); 8.10 (d, 2H).

**N-[4'-(Methacryloxy)butyl] Carbazole (2b).** Yield: 86%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.67-1.81 (m, 2H); 1.92-2.06 (m, 5H); 4.16 (t, 2H); 4.35 (t, 2H); 5.54 (m, 1H); 6.06 (m, 1H); 7.18-7.29 (m, 2H); 7.36-7.50 (m, 4H); 8.12 (d, 2H).

**N-[5'-(Methacryloxy)pentyl] Carbazole (2c).** Yield: 78%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.39-1.56 (m, 2H); 1.63-1.77 (m, 2H); 1.85-2.01 (5H); 4.10 (t, 2H); 4.31 (t, 2H); 5.51 (m, 1H); 6.03 (m, 1H); 7.16-7.29 (m, 2H); 7.35-7.54 (m, 4H); 8.10 (d, 2H).

**N-[6'-(Methacryloxy)hexyl] Carbazole (2d).** Yield: 75%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.38-1.45 (m, 4H); 1.67 (m, 2H); 1.84-1.94 (m, 5H); 4.11 (t, 2H); 4.30 (t, 2H); 5.54 (m, 1H); 6.09 (m, 1H); 7.17-7.31 (m, 2H); 7.38-7.52 (m, 4H); 8.12 (m, 2H).

**N-[8'-(Methacryloxy)octyl] Carbazole (2e).** Yield: 62%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.33 (m, 8H); 1.58-1.68 (m, 2H); 1.77-1.96 (m, 5H); 4.14 (t, 2H); 4.29 (t, 2H); 5.56 (m, 1H); 6.12 (m, 1H); 7.22-7.29 (m, 2H); 7.37-7.52 (m, 4H); 8.13 (d, 2H).

**N-[9'-(Methacryloxy)nonyl] Carbazole (2f).** Yield: 61%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.34 (m, 10H); 1.62-1.75 (m, 2H); 1.81-2.01 (m, 2H); 4.17 (t, 2H); 4.30 (t, 2H); 5.58 (m, 1H); 6.17 (m, 1H); 7.20-7.33 (m, 2H); 7.35-7.56 (m, 4H); 8.15 (d, 2H).

**N-[10'-(Methacryloxy)decyl] Carbazole (2g).** Yield: 62%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.22 (m, 12H); 1.57 (t, 2H); 1.80 (t, 2H); 1.86 (s, 3H); 4.05 (t, 2H); 4.23 (t, 2H); 5.46 (t, 1H); 6.02 (t, 1H); 7.15 (m, 2H); 7.36 (m, 4H); 8.03 (d, 2H).

### **Preparation of 4''-Nitrophenyl-3-[N-[ $\omega$ '-(Methacryloxy)alkyl]] Carbazolyl diazenes (3a-3g)**

4-Nitroaniline (2.0 g, 14 mmol) and con. HCl (8 ml) were added in 200 ml of water. The mixture was cooled in an ice bath and a solution of sodium nitrite (1.2 g, 17 mmol) in water (10 ml) was added slowly to the 4-nitroaniline solution. The mixture was allowed to stir in the ice bath for 30 min., while the yellow solution became colourless. Sodium dodecylbenzenesulphonate (NaDBS) (1.0 g) was then added to the mixture and the mixture was stirred vigorously at 3 °C for 15 min. N-[ $\omega$ '-(methacryloxy)alkyl] carbazole (30 mmol) dissolved in 225 ml dichloromethane was dropwise added to the reaction mixture. The reactant mixture was stirred vigorously at room temperature for 48 hours. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography. Pure products were obtained after removing the solvent under reduced pressure.

**4''-Nitrophenyl-3-[N-[3'-(Methacryloxy)propyl]] Carbazolyl Diazene (3a).** Yield: 10%, mp 78°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.96 (s, 3H); 2.15-2.37 (m, 2H); 4.17 (t, 2H); 4.49 (t, 2H); 5.61 (m, 1H); 6.12 (m, 1H); 7.25-7.35 (m, 1H); 7.41-7.56 (m, 3H); 8.12-8.19 (m, 2H); 8.33-8.40 (m, 2H); 8.73 (d, 1H).

**4''-Nitrophenyl-3-[N-[4'-(Methacryloxy)butyl]] Carbazolyl Diazene (3b).** Yield: 12%, mp 75°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.70-1.84 (m, 2H); 1.90-2.06 (m, 5H); 4.18 (t, 2H); 4.40 (t, 2H); 5.54 (m, 1H); 6.05 (m, 1H); 7.21-7.56 (m, 4H); 8.00-8.19 (m, 4H); 8.33-8.38 (m, 2H); 8.73 (d, 2H).

**4''-Nitrophenyl-3-[N-[5'-(Methacryloxy)pentyl]] Carbazolyl Diazene (3c).** Yield: 11%, mp 72°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.40-1.554 (m, 2H); 1.65-1.79 (m, 2H); 1.87-2.10 (m, 5H); 4.11 (t, 2H); 4.37 (t, 2H); 5.50 (m, 1H); 6.01 (m, 1H); 7.27-7.56 (m, 4H); 8.01-8.19 (m, 4H); 8.35-8.40

(m, 2H); 8.74 (d, 2H).

**4''-Nitrophenyl-3-[N-[6'-(Methacryloxy)hexyl]] Carbazolyl Diazene (3d).** Yield: 14%, mp 70°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.41-1.48 (m, 4H); 1.58-1.69 (m, 2H); 1.82-1.89 (m, 5H); 4.12 (t, 2H); 4.37 (t, 2H); 5.54 (m, 1H); 6.08 (m, 1H); 7.29-7.58 (m, 4H); 8.03-8.21 (m, 4H); 8.36-8.43 (m, 2H); 8.75 (d, 2H).

**4''-Nitrophenyl-3-[N-[8'-(Methacryloxy)octyl]] Carbazolyl Diazene (3e).** Yield: 12%, mp 69°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.25 (m, 8H); 1.48-1.62 (m, 2H); 1.76-1.90 (m, 5H); 4.04 (t, 2H); 4.26 (t, 2H); 5.45 (m, 1H); 6.00 (m, 1H); 7.21-7.50 (m, 4H); 7.89-8.12 (m, 4H); 8.25-8.32 (m, 2H); 8.66 (d, 2H).

**4''-Nitrophenyl-3-[N-[9'-(Methacryloxy)nonyl]] Carbazolyl Diazene (3f).** Yield: 9%, mp 67°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.24 (m, 10H); 1.46-1.63 (m, 2H); 1.79-1.91 (m, 5H); 4.09 (t, 2H); 4.28 (t, 2H); 5.42 (m, 1H); 6.01 (m, 1H); 7.21-7.49 (m, 4H); 7.87-8.09 (m, 4H); 8.21-8.30 (m, 2H); 8.68 (d, 2H).

**4''-Nitrophenyl-3-[N-[10'-(Methacryloxy)decyl]] Carbazolyl Diazene (3g).** Yield: 16%, mp 79°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.28 (m, 12H); 1.56 (t, 2H); 1.93 (m, 5H); 4.12 (t, 2H); 4.36 (t, 2H); 5.53 (s, 1H); 6.08 (s, 1H); 7.26 (m, 2H); 7.48 (m, 2H); 8.06 (d, 2H); 8.12 (m, 2H); 8.40 (d, 2H); 8.77 (d, 1H).

**Polymerization of Monomers (3a-3g): Preparation of Poly-[Nitrophenyl-[3-[N-[ω'-(Methacryloxy)alkyl]] Carbazolyl Diazene].**

The polymerization for all the monomers was carried out in 1,2-dichlorobenzene with 10% 2,2'-azobisisobutyronitrile (AIBN) as initiator. The reaction solution was purged with argon

for 30 min. and sealed. The monomer was allowed to polymerize under argon at 60 °C for two days. The polymerization was stopped by precipitating the reaction solution in ethanol. The polymer was obtained by filtration and purified by reprecipitation the polymer solution from THF into ethanol, and dried under vacuum. The preparation of the azo-carbazole polymer with an ethylene spacer was published previously.<sup>17</sup>

### Sample Preparation

The n-variable spacer poly(azo carbazole) (PAC-n) polymers used in this study were cast as films onto transparent substrates, either cleaned glass microscope slides, or Indium-Tin-Oxide (ITO)-coated glass when an electrically conductive substrate was required. For studies of photoinduced orientation, spin-cast films on glass were prepared; for determination of photoconductivity and poling dynamics the polymer was 'sandwiched' between two ITO plates so that an electric field could be applied normal to the substrate; and for optical gain coupling polymer cells were cast in etched channels of ITO on glass, so that an electric field could be applied parallel to the substrate.

To produce thin films, the polymers were dissolved in tetrahydrofuran (THF), spin-cast onto clean glass substrates, and heated to  $T_g + 10$  °C to yield dry amorphous films of good optical quality and of thickness between 200 and 400 nm.

For EO sandwich samples, ITO-coated glass substrates were masked with tape and the exposed ITO was dissolved in a concentrated HCl/HNO<sub>3</sub> acid bath to remove all of the ITO

except for a 2 mm-wide strip centred on the substrate, and then cleaned with distilled water and methanol. Dry powdered polymer was deposited on the ITO strip, and a second etched substrate placed on top of the first, inverted and rotated such that the two ITO strips were adjacent to the polymer with an area of intersection of  $\sim 4 \text{ mm}^2$ . The samples were heated to a temperature of  $T_g + 30^\circ$  for 2 hours while applying a force of  $\sim 100 \text{ g/cm}^2$  on the top plate, and then cooled slowly to room temperature over 4 hours. This yielded polymer sandwiches of good optical quality, of a thickness between 1 and  $10 \text{ }\mu\text{m}$ , and with electric plates on both sides of the film which could be addressed to apply a field across the polymer normal to the plane of the film. Film thickness of the sandwiches was determined by optical absorbance, relative to the corresponding thin film where thickness could be determined directly by interferometry.

To produce polymer EO cells, ITO-coated glass substrates were similarly acid-etched to yield ITO strips running the width of the substrate, with a width of 4 mm, and a narrow ( $\sim 150 \text{ }\mu\text{m}$ ) channel etched midway. Polymer dissolved in THF was deposited into this  $0.15 \text{ mm} \times 4 \text{ mm}$  cell, and slow-evaporated to yield a laterally-ITO-bound electro-optic polymer cell of good optical quality with a thickness between 600 nm and 1200 nm. Electrodes were attached to the exposed ends of the ITO fingers so that an electric field could be applied across the polymer film parallel to the plane of the substrate. Thickness was determined by interferometry of the polymer film directly adjacent to the cell, and the cell width was determined by optical microscopy with a linearly-ruled distance scale. The three types of cast films are depicted in Figure 1.

*FIGURE 1.*

## Optical Characterization

Induced order in the polymer samples was measured by photo-inducing birefringence similar to methods described previously,<sup>1</sup> where a 633 nm probe beam was attenuated to 0.01 mW, linearly polarized 45° off-axis, and introduced normal to the polymer thin films which were placed between crossed polarizers oriented along and against the axis of probe beam polarization. The intensity of the light passing through crossed polarizers and into a photomultiplier tube was then monitored over time while birefringence was induced in the sample by a 3 mW pump (or 'writing') beam at 488 nm linearly polarized on-axis from an Ar<sup>+</sup> laser, coincident with the probe beam on the sample. The writing beam polarization could be modulated with a Pockels cell to switch from linear (for writing birefringence) to circular (to erase) polarizations.

Photoconductivity of the PAC-n polymer series was determined as described,<sup>19</sup> by measuring the difference between the dark current and that resulting from 2 mW/mm<sup>2</sup> 633 nm laser irradiation of the sample with a 50 V/μm applied voltage.

Optical characterization of the photorefractive effect was conducted in the red region at 633 nm so as to minimize the competition between PR gratings and birefringence gratings (which are of much lower efficiency when inscribed at 633 nm) and between PR gratings and surface relief gratings (which have not been observed with a 633 nm writing wavelength). To further characterize photorefractivity unambiguously, the PR effect was measured by two-beam optical gain coupling as opposed to PR grating diffraction efficiency, as the PR effect is the only mechanism that could be responsible for asymmetric beam coupling.<sup>7</sup> Electro-optic polymer cells were placed in an oven and heated to  $T_g + 20^\circ$  over 30 min. A DC field of 15 V/μm was

then applied for 90 min at this temperature, and maintained while the sample was cooled back down to room temperature over a further 90 min before removal. The cells were then immediately placed in an optical setup similar to that described in the literature.<sup>7,20</sup> Two 633 nm *s*-linearly polarized writing beams of equal power at 1.5 mW were focussed to ~200  $\mu\text{m}$  in diameter and coincided in the cell to produce an interference pattern with  $2\theta = 46^\circ$ . The beams could be selectively removed and introduced with a manual shutter, and the intensity of either beam measured with a photodiode and recorded. To measure asymmetric gain or loss, the intensity of one beam was recorded while the second was introduced and removed, then the same procedure carried out for the second beam while the first was removed and then reintroduced.

## Results and Discussion

The azobenzene-based polymers comprise an eight-member series of poly(azo carbazole) polymers (PAC-*n*), linked to a methacrylate backbone by a spacer of variable length (*n*) from 2 to 10 methylene units. The results of glass transition temperature determination, average *MW* determination, and optical characterization are shown in Table 1.

TABLE 1.

It is clear that there does not appear to be a significant difference in the absorbance maxima of the samples, as the  $\lambda_{\text{max}}$  values for all samples are contained within a range of 440 to

450 nm, nor does there appear to be a significant variation in the extinction coefficients. One might expect a slight decrease in the extinction coefficients with increasing spacer length, due to a decrease in the relative concentration of the absorbing chromophores across the series, from 'dilution' in the bulk with the methylene units. This relative chromophore dilution would be expected to be near 20% from the PAC-2 to the PAC-10 polymer. This trend is consistent with the  $\epsilon$  data in Table 1, as far as the experimental uncertainty of  $\pm 10\%$  (due to the determination of film thickness) allows a comparison. The absence of other apparent trends in the  $\lambda_{\max}$ ,  $\epsilon_{445}$ , and  $\epsilon_{633}$  results suggests that there is not an appreciable variation in the electronic environment of the chromophores across the series, and that the azo chromophores can be considered to be in a similar electronic environment for all polymers in the series.

A distinct trend is clear from the  $T_g$  values presented in Table 1, as the  $T_g$  is depressed by more than 100 degrees with the increase in the number of chain spacers from 2 to 10 methylene units. This suggests that there is a substantial increase in the mobility across the series from the PAC-2 to the PAC-10 polymers, and that this is most pronounced at short spacer lengths. A difference in  $T_g$  of only 5 degrees is observed between the 3 samples with the longest methylene spacers of  $n = 8, 9$ , and  $10$ , which is within the experimental uncertainty of  $T_g$  determination and the inherent range of the transition itself. These  $T_g$  values are in agreement with the characterization results of a similar series of poly(*n*-methylene carbazole) photorefractive polymers, where an increase in the length of methylene spacer between a carbazole moiety and methacrylate backbone from 2 to 11 units resulted in a  $T_g$  decrease from 148 °C to 31 °C.<sup>21</sup> In another similar study with main chain carbazole-based polymers,<sup>18</sup> extension of an alkyl chain pendant on the carbazole group (introduced to lower  $T_g$ ) from 6 to 13 methylene units depressed

the  $T_g$  to 53 °C from 87 °C.

In examining the dependence on the mobility of optical and electro-optic effects, it would be reasonable to expect that the most pronounced influence would be on the phenomena which involve reorientation of the side groups in the polymer matrix, such as electric field poling and photoinduced birefringence. Once an electro-optic thin film sandwich of azo polymer is brought to  $T_g$ , application of an electric field across the film induces poling and aligns the dipoles with the applied electric field, as measured by the birefringence between crossed polarizers while a poling field of 50 V/ $\mu\text{m}$  was applied to the samples at  $T_g + 20^\circ$ . The poling rates for all of the samples appeared to be similar, though low signal-to-noise ratios in these films precluded a quantitative comparison.

A more useful comparison of orientational dynamics across the polymer series can be made at room temperature by photoinducing orientation with a linearly polarized laser, as this technique can induce a high degree of orientational order in all of the samples under the same conditions, and with a high-enough signal-to-noise ratio to collect data of a resolution suitable for curve fitting. Since these experiments were carried out at room temperature, below the  $T_g$  of all of the polymers (unlike high temperature poling), this also allows an observation of the residual stable birefringence that remains in the samples after the orienting laser light is removed.

A typical photoinduced birefringence writing curve (that of a PAC-5 film) is displayed in Figure 2, where linearly polarized light is introduced to the thin film at time  $t = 10$  seconds to induce birefringence, and removed at time  $t = 60$  seconds. At time  $t = 370$  seconds circularly polarized light of the same wavelength is introduced to erase the birefringence. At time  $t = 60$  seconds when the writing laser is removed, there is a relaxation from the saturation level of birefringence

on the order of hundreds of seconds, and the orientation that remains after this time is stable temporally until the introduction of circularly polarized light at time  $t = 370$  seconds or until the sample is heated up to  $T_g$ .

*FIGURE 2.*

The maximum levels of birefringence which could be induced in each sample in the series are listed in Table 1. From previous studies of photoinduced birefringence in similar azobenzene polymers,<sup>22,23</sup> it has been shown that the growth section of the curve depicted in Figure 2 can be modelled effectively with a biexponential equation

$$\Delta n / \Delta n_{max} = A(1 - \exp(-t/t_a)) + B(1 - \exp(-t/t_b)) \quad (1)$$

where  $A$  and  $B$  are normalized constants ( $A + B = 1$ ) describing the relative contributions of two exponential growth functions described by characteristic time constants  $t_a$  and  $t_b$ . If  $t_a < t_b$ , then these can be regarded as the time constants for a fast and slow growth rate respectively, with a fast rate coefficient  $A$  and a slow rate coefficient  $B$ . Similarly, the relaxation section of the birefringence curves depicted in Figure 2 can be closely approximated with a biexponential decay equation

$$\Delta n / \Delta n_{max} = C \exp(-t/t_c) + D \exp(-t/t_d) + E \quad (2)$$

where  $C$  and  $D$  are coefficients describing the fast and slow exponential relaxations with characteristic time constants of  $t_c$  and  $t_d$  when  $t_c < t_d$ .<sup>22,23</sup>  $E$  represents the fraction of the induced birefringence which is stable over time, and  $C$ ,  $D$ , and  $E$  are also normalized. Using Equations (1) and (2), both the growth and the relaxation curves for all samples were fit to determine the dimensionless coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$ ; and the characteristic time constants  $t_a$ ,  $t_b$ ,  $t_c$ , and  $t_d$  in seconds. The fitted biexponential curves lay within the experimental noise recorded by the probe beam detection equipment, and results of this curve fitting are presented in Table 2. Error estimates for the fits of the data to Equations (1) and (2) were observed to be similar to those presented in previous curve-fitting publications.<sup>22,23</sup>

TABLE 2.

From examination of these component coefficients it is obvious that the orientation process is dominated by one time constant, that of the fast process. In the relaxation process both the fast and the slow components make an appreciable contribution, though that of the slower component is dominant. From the values of  $t_a$  and  $t_d$  it is clear that there is a definite trend towards a shorter time constant (and hence faster process) for both the growth and relaxation components, by nearly 50% in both cases, as the spacer length in the polymers is increased from 2 to 10 methylene units. This can be attributed to the increased mobility of the side chains, as both of these processes involve substantial motion of the pendant chromophores within the bulk polymer matrix.

This trend is also apparent when one examines the levels of birefringence which can be

induced at saturation (maximum  $\Delta n$ ), and that which remains after relaxation ( $E$ ). It is apparent that in addition to a faster rate, the levels of maximum and stable birefringence decrease significantly over the series as well. A strong suggestion that this dependence is due mainly to a mobility-enhancement and  $T_g$  depression becomes evident when the  $\Delta n$  and  $E$  data are plotted against  $(T - T_g)$ , the difference between the experimental temperature and the glass transition temperature for each sample. These  $\Delta n$  vs  $\Delta T$  plots are presented in Figure 3 and Figure 4. The experimental uncertainty for the  $\Delta n$  measurements was  $\pm 10\%$ .

*FIGURE 3 and FIGURE 4.*

What is useful to note from this treatment of the data is that the shape of the maximum and stable birefringence vs  $\Delta T$  curves bears resemblance to induced-order vs  $T$  plots for single poled polymer samples over a range of temperatures which have been fit to a master curve of orientational decay.<sup>24</sup> Although this master curve describes the iso-thermal relaxation rate of poled order, and the observations here plotted here are of birefringence over temperature, the results are similar with respect to the general shape: as  $T_g$  is approached there is a sharp decrease in the orientation towards zero, as the equilibrium between the induced order and the thermal disorder is shifted towards disordering with increasing  $kT$ . This suggests that the maximum and stable levels of birefringence for the PAC-n series might all lie on a similar master curve and exhibit similar behavior, once corrected for this temperature difference. This is further supported by the observation that when the electric field poling was carried out on the PAC-n samples 'temperature corrected' to  $T_g + 20^\circ$ , there was not a significant variation in rate or extent across

the series. From these results it is clear that while orientation is more readily induced in polymers with a lower  $T_g$ , this advantage is overcome by the associated increase in thermal relaxation. The net effect of this appears to be that materials with the lowest mobility (those with the highest  $T_g$ ) possess the potential for both the highest level of order which can be photoinduced, and the greatest retention (lowest fraction of relaxation) of this induced order.

The photoconductivity ( $\Phi$  in A/V·cm) of the polymer thin films was determined as described for all of the PAC-n polymers, and results are presented in Table 1. Although not as pronounced a trend as that of the induced birefringence, the data are consistent with a decrease in the photoconductivity over the series as the spacer length is increased. The experimental uncertainty in these measurements is equal to  $\pm 2.5 \times 10^{-14}$  A/V·cm. As discussed, there is likely a decrease in the chromophore density across the series, and hence a comparison between the samples corrected for film thickness might not be as meaningful as a comparison correcting for the effective optical path length to account for chromophore dilution. This dilution effect would amount to ~20% across the series however, in comparison to a ~30% decrease in  $\Phi$  from the PAC-2 to the PAC-10 polymers:

After the samples are cast into EO cells and poled, photorefractive gratings can be inscribed by the method described. Films of these azobenzene polymers have been shown to be suitable materials for inscription of a variety of holographic gratings (such as isomerization, birefringence, and surface relief),<sup>5,6</sup> so four-wave mixing experiments to measure the photorefractive effect by diffraction efficiency would not be conclusive. Two-beam optical gain coupling at 633 nm was used to probe the formation of the photorefractive gratings, as it can be the only source of such an effect. While the  $\lambda_{\text{max}}$  of these polymers is in the UV and blue-visible

range, there is still an appreciable absorption tail at 633 nm where measurements are taken. It was observed that this absorption by the gratings serves to reorient the poled chromophores by a weak isomerization and photo-orientation mechanism, (especially at the high light intensities necessary for an appreciable photoconductive response), and erases the gratings with a timescale of minutes. Hence for these experiments two-beam coupling (2BC) was performed directly after poling, and the gain was recorded directly after PR grating inscription so as to minimize this erasure by the probe beam, and to compare effectively samples which display varying rates of poled order decay at room temperature. A typical 2BC optical gain experiment is depicted in Figure 5 for a PAC-5 EO cell.

*FIGURE 5.*

The low signal-to-noise ratio illustrates that measurements at lower poling fields, lower irradiation intensities, or during relaxation could not easily be made, and the 15 v/ $\mu\text{m}$  poling field used for all samples represents the highest electric field that could be presented to the material before dielectric breakdown.

The two baselines represent the intensities of the two writing beams over the course of two consecutive experiments. The upper trace depicts the intensity of the first beam, and the lower trace the intensity of the second. With the first beam on, at time  $t = 13$  seconds the other beam is introduced, and removed at time  $t = 27$  seconds. The amount of increase (optical gain) of intensity of this beam is at the expense of a decrease (optical loss) in the other, and the optical gain can be estimated from this as  $0.026 \mu\text{m}^{-1}$ . As there are other possible mechanisms for

producing optical gain,<sup>20</sup> the amount of loss of the second beam ( $0.022\ \mu\text{m}^{-1}$ ) is used as an unambiguous measure of the PR gain of the first, since photorefractivity is the only mechanism that could be responsible for the asymmetric loss in these systems.<sup>7</sup> Non-PR gain during 2BC can arise from a variety of sources, including scattering of the second beam into the detector of the first beam, or increasing the transmittance of the sample by altering the *cis/trans* isomeric ratio in the photostationary state.<sup>20</sup> The loss observed in these gratings was always of a lesser magnitude than the gain, so it is likely that some of these other non-PR gain effects are occurring simultaneously in these films. Two-beam coupling gain was not observed with unpoled samples, or with PR gratings that had been erased by high intensity exposure at 633 nm for 30 minutes. In this fashion the 2BC optical gain was determined for all PAC-n samples, and the results are presented in Figure 6.

*FIGURE 6.*

Although the magnitude of the experimental uncertainty ( $\pm 30\%$ ) precludes a clear trend to be discerned, it appears that the samples with the longer spacers suffer a decrease in optical gain. This could be due to the photoconductivity decrease with increasing *n* as shown by the  $\Phi$  values in Table 1, and it could also represent a decreased EO effect in addition to decreased charge transfer, as the higher *n* samples near  $T_g$  would likely suffer a greater loss of poled order due to relaxation and hence a decreased EO response. It is also possible that a mobility-dependent orientational enhancement of the optical gain is being observed.

While the carbazole/azobenzene-functionalized polymers possess a number of advantages

as photorefractive materials such as high component concentration, sensitizer-free charge generation, internal field generated EO response, and versatility such as the potential for optically-assisted poling, these materials also present a number of disadvantages to their application as PR holographic polymers. Foremost, the gain would have to be increased in order to exceed losses due to the strong optical absorption tail extending deep into the red ( $\epsilon_{633} > 2200 \text{ cm}^{-1}$ ) for net gain to be realized with two-beam coupling. This absorption loss of  $0.2 \mu\text{m}^{-1}$  is still an order of magnitude above the 2BC gain observed here of  $\sim 0.02 \mu\text{m}^{-1}$ , so that at present no net gain is possible. This absorption also limits the thickness of the samples optically to a maximum of tens of micrometers when irradiating with light at 633 nm, which is still an order of magnitude thinner than any PR polymers which have been shown to produce a 'useful' gain of  $>100\%$  or more,<sup>25</sup> and this absorption appears to erase the grating during the reading process by a weak isomerization and subsequent photo-orientation process. The two-beam coupling results do demonstrate however that the  $T_g$  of single-component multi-functional photorefractive polymers can be tailored over a range greater than  $100^\circ$ , without a significant change in the photorefractive effect.

## Conclusions

A series of amorphous single-component multi-functional azo-carbazole polymers in which the electro-optic side chains are attached to a methacrylate backbone by spacers of various lengths was prepared and characterized, and substantial differences were observed in the rates

and extent of photoinduced birefringence and orientational relaxation between the samples. Polymers of the highest  $T_g$  displayed both the highest level of order which could be induced, and the greatest fraction of this order that could be retained after orientational relaxation. A photorefractive two-beam optical gain of  $0.024 \mu\text{m}^{-1}$  was demonstrated in films of the polymer with the highest glass transition temperature, although this was exceeded by absorption losses of the polymer, so that no net gain could be recorded at 633 nm.

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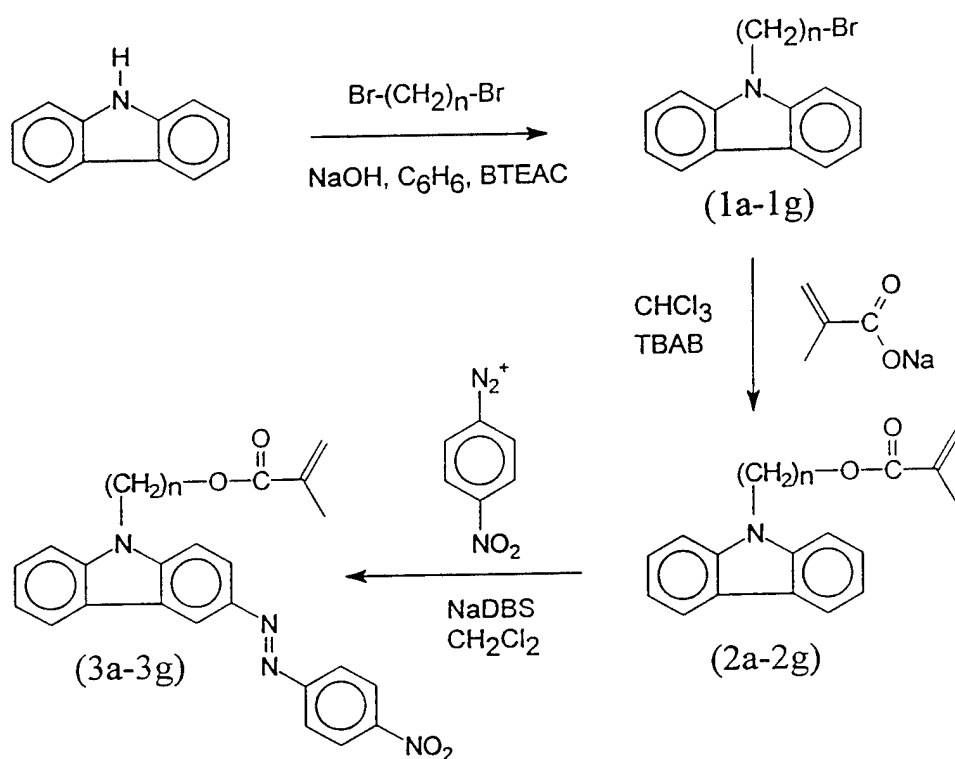
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## Table and Figure Captions

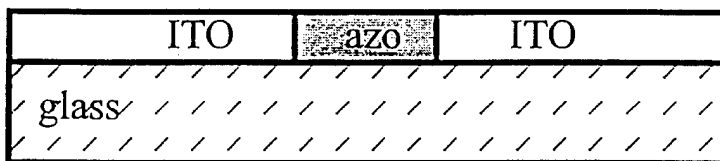
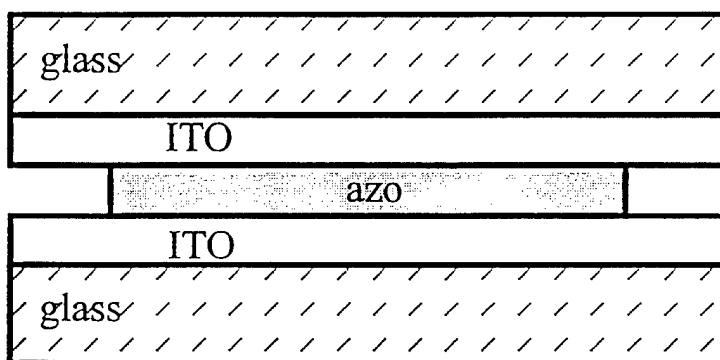
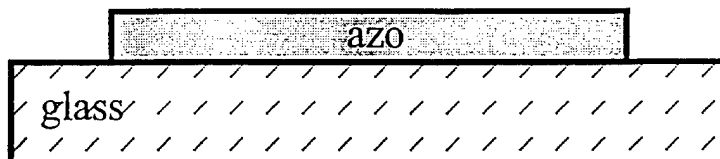
- Table 1. Physical and optical characteristics of the PAC-n polymer series.
- Table 2. Time constants and coefficients obtained from curve fitting.
- Figure 1. Azo-carbazole polymer cast as a thin film (top), an electro-optic sandwich (center), and an electro-optic cell (bottom).
- Figure 2. Photoinduced and erased birefringence in a PAC-5 polymer thin film.
- Figure 3. Maximum level of birefringence photoinducible vs  $(T-T_g)$ .
- Figure 4. Fraction of photoinduced birefringence remaining after relaxation vs  $(T-T_g)$ .
- Figure 5. Change in beam intensity to demonstrate asymmetric two beam coupling in a PAC-5 photorefractive grating. Top: intensity of beam 1, and bottom: intensity of beam 2, as the other beam is introduced and removed.
- Figure 6. Optical gain achievable for the PAC-n photorefractive polymers.

n	$T_g$ (°C)	$T_{dec}$ (°C)	$MW$ (g/mol)	$\lambda_{max}$ (nm)	$\varepsilon_{445}$ ( $\mu\text{m}^{-1}$ )	$\varepsilon_{633}$ ( $\mu\text{m}^{-1}$ )	$\Delta n$	$\Phi$ (A/V·cm)
2	167	286	9200	444	3.9	0.27	0.065	$2.8 \times 10^{-13}$
3	127	288	3600	440	3.8	0.26	0.064	$2.1 \times 10^{-13}$
4	99	293	4200	443	4.2	0.29	0.058	$2.5 \times 10^{-13}$
5	88	289	4450	447	3.5	0.24	0.053	$2.0 \times 10^{-13}$
6	81	285	3600	450	3.2	0.22	0.054	$1.7 \times 10^{-13}$
8	70	298	6200	445	3.7	0.26	0.045	$2.1 \times 10^{-13}$
9	69	295	4700	443	3.8	0.26	0.051	$1.7 \times 10^{-13}$
10	65	282	6200	445	3.7	0.26	0.042	$1.9 \times 10^{-13}$

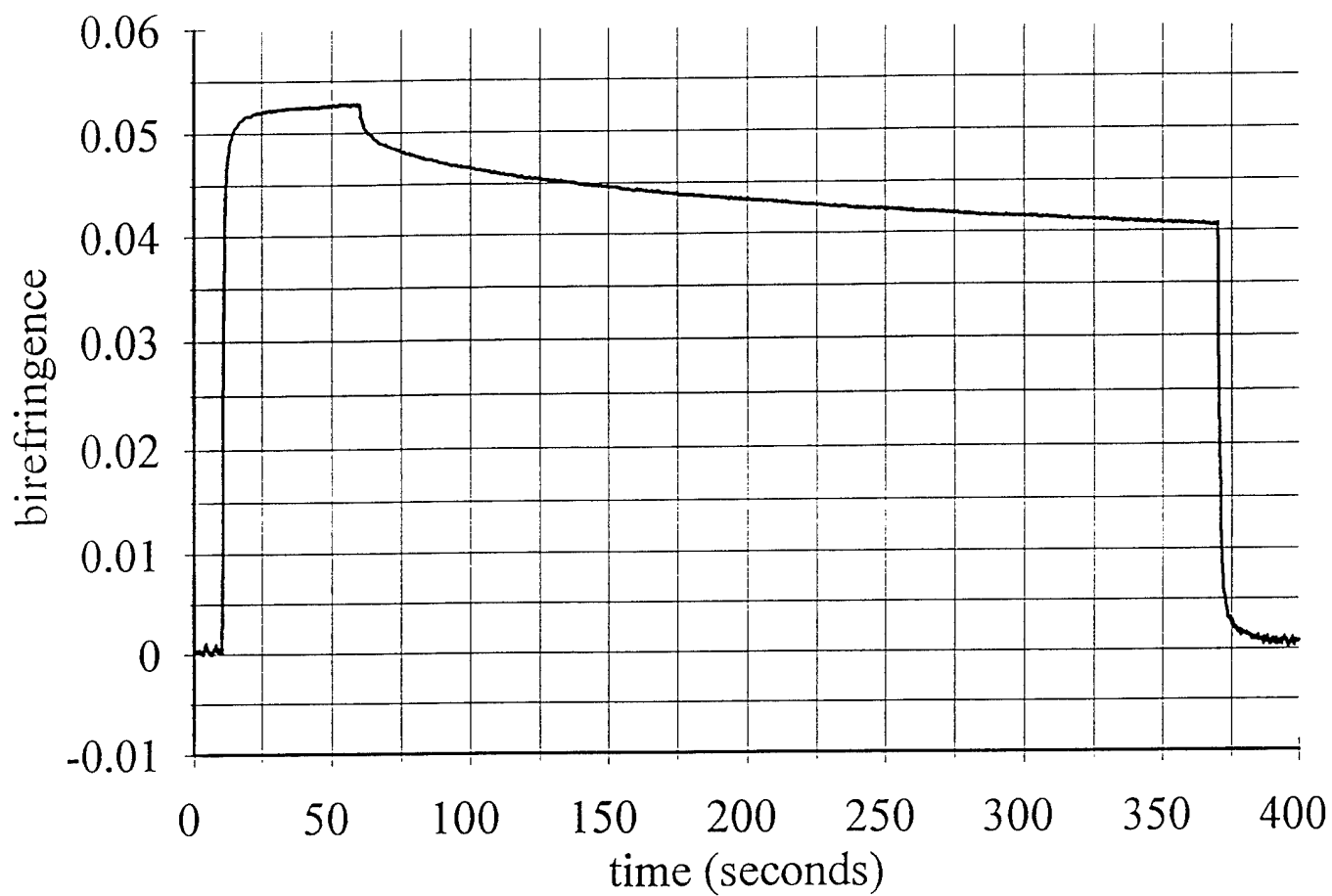
n	$A$	$t_a$ (s)	$B$	$t_b$ (s)	$C$	$t_c$ (s)	$D$	$t_d$ (s)	$E$
2	0.87	0.78	0.13	7.77	0.06	4.28	0.16	205	0.78
3	0.92	0.65	0.08	6.40	0.05	5.11	0.15	202	0.80
4	0.92	0.77	0.08	11.0	0.10	3.41	0.19	168	0.72
5	0.92	0.67	0.08	9.00	0.08	3.80	0.17	153	0.75
6	0.93	0.63	0.07	8.42	0.09	3.84	0.22	157	0.69
8	0.95	0.50	0.05	7.77	0.11	3.77	0.25	153	0.64
9	0.95	0.57	0.05	15.8	0.12	3.56	0.26	136	0.62
10	0.97	0.47	0.03	35.6	0.16	2.63	0.29	131	0.55



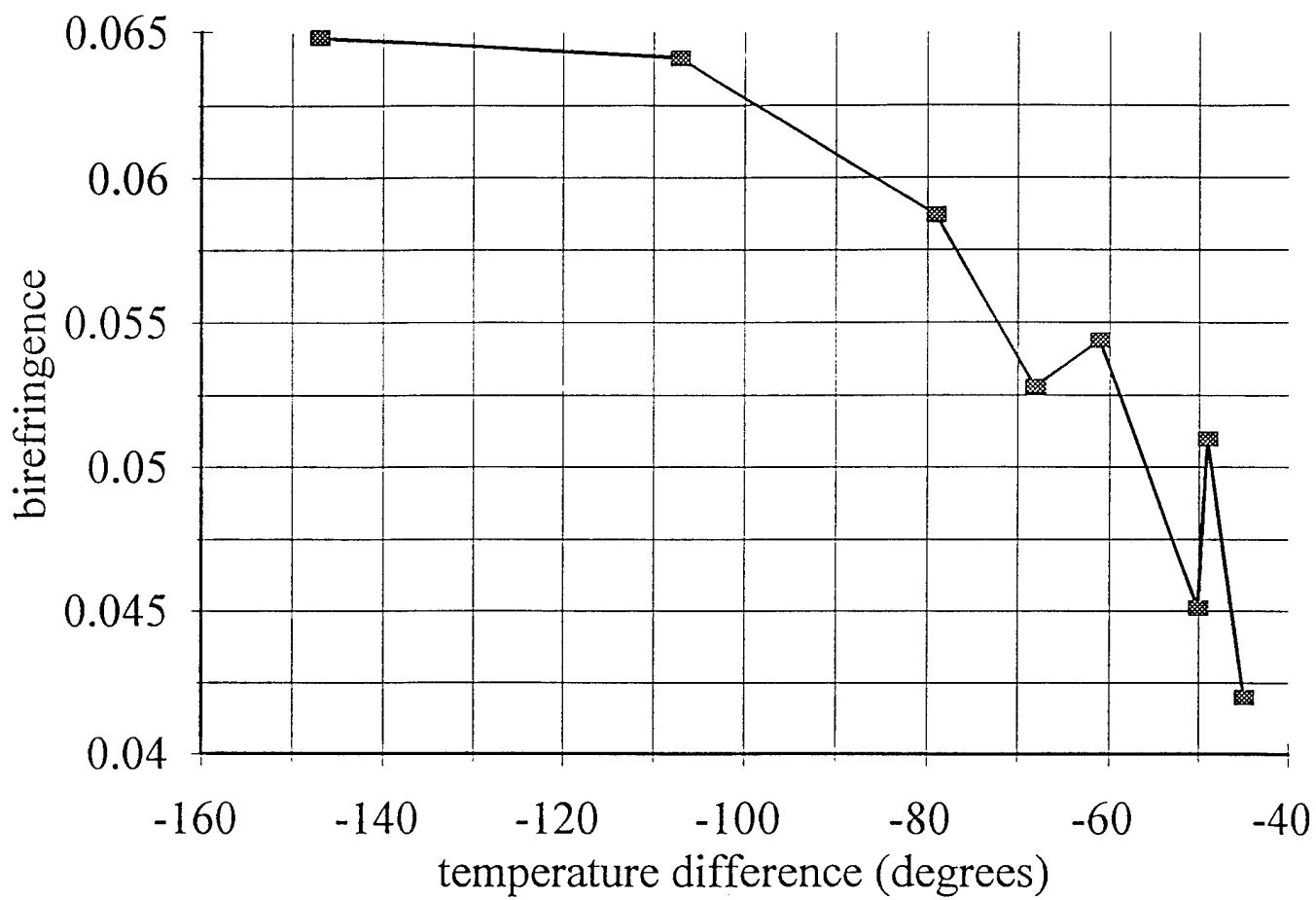
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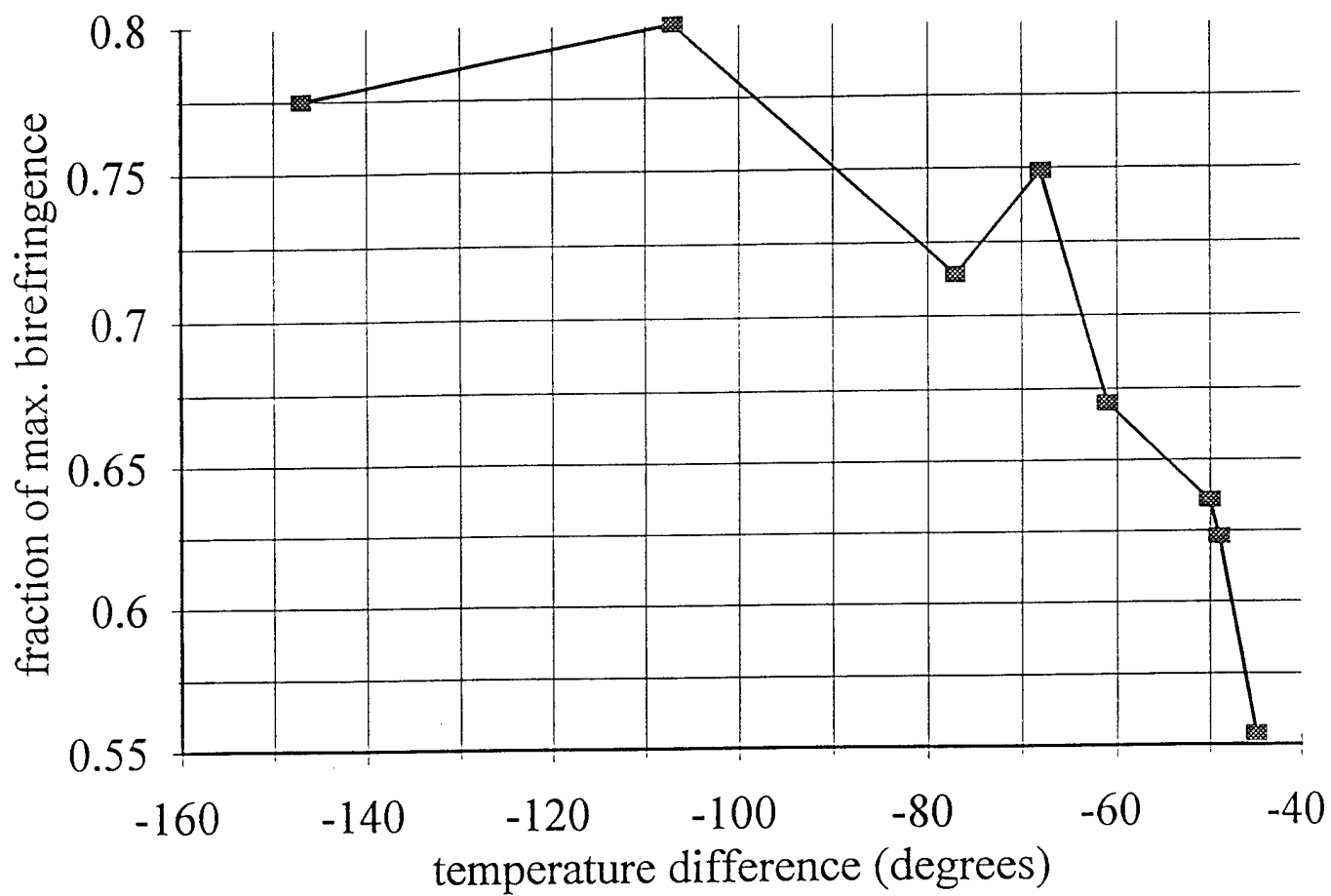
Barrett Figure 1



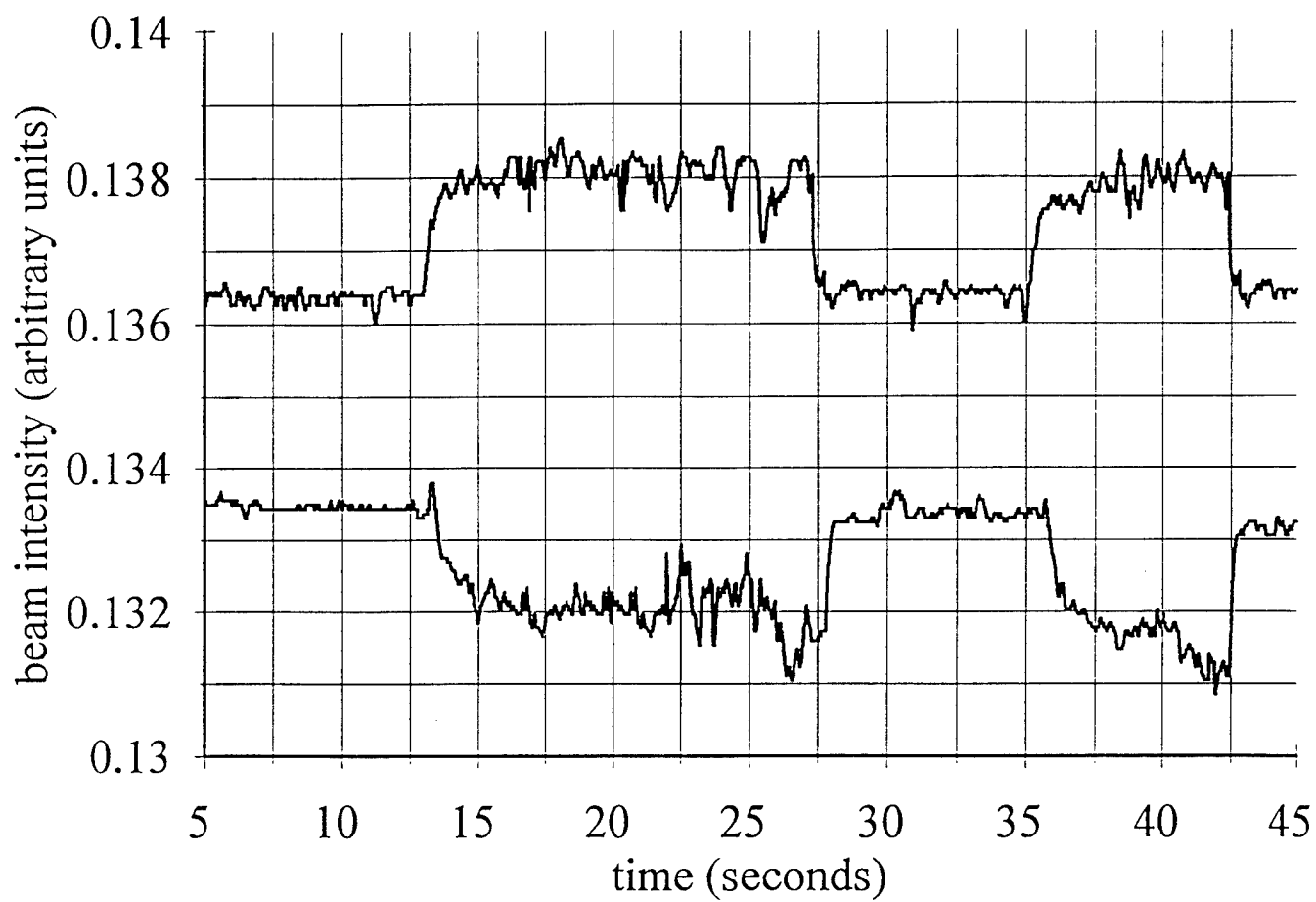
Same Figure 2



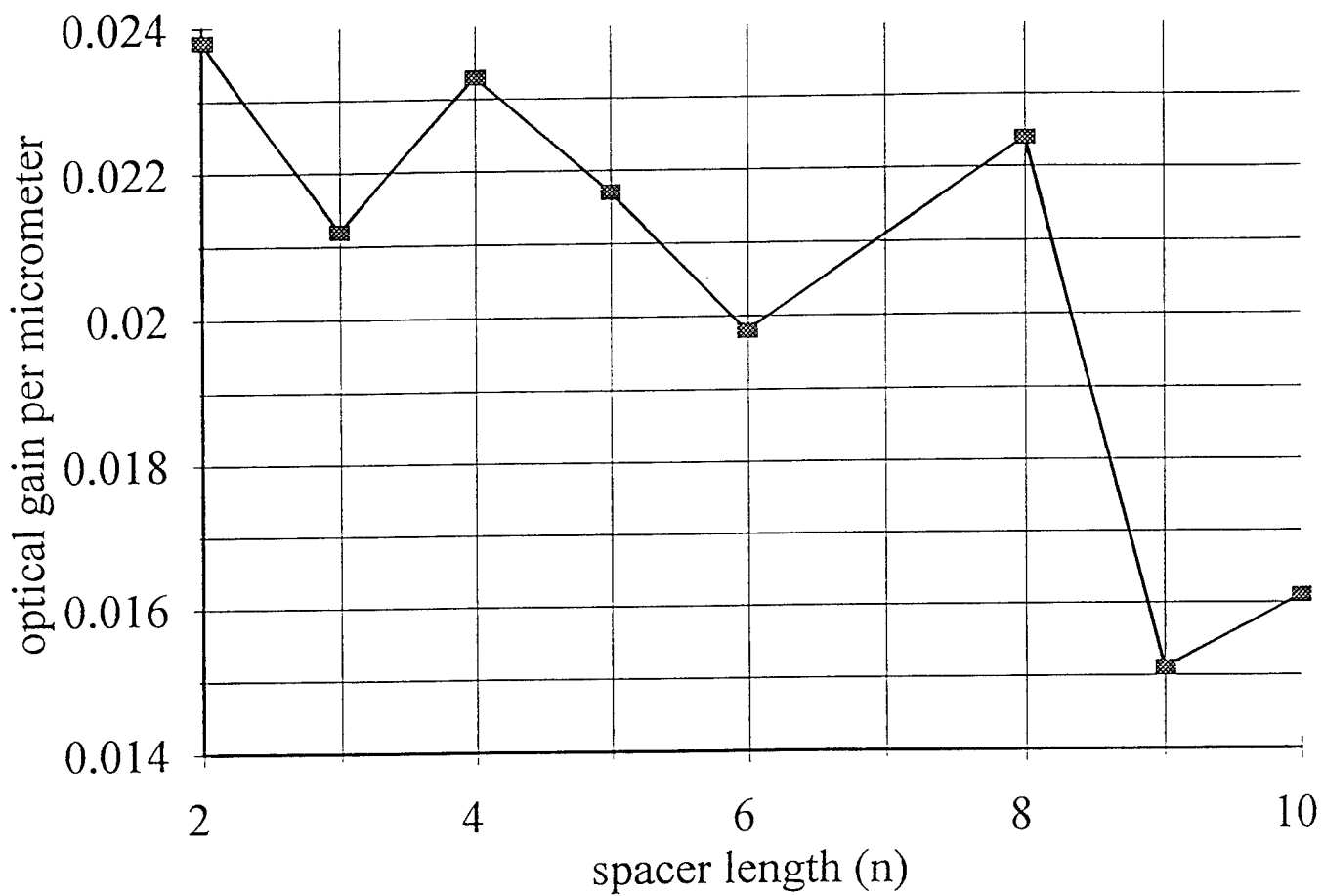
Case - figure



Barre 2 Figure 2



Carroll Figure 15



Source: Figure 16